

THE ROTATIONAL SPECTRUM OF THE C₃H RADICALC. A. GOTTLIEB, E. W. GOTTLIEB, P. THADDEUS, AND J. M. VRTILEK¹

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ABSTRACT

The rotational spectrum of the recently discovered C₃H radical in both fine-structure ladders of its electronic ground state ($X^2\Pi$) with lambda doubling and hyperfine structure has been determined to high accuracy, and the strongest transitions at frequencies less than 376 GHz are tabulated. Recently published spectroscopic constants derived from astronomical and laboratory data (Gottlieb *et al.* 1985) allowed calculation of the spectrum to a radial velocity of 0.4 km s⁻¹ at frequencies less than 200 GHz, the uncertainties above being somewhat larger. The hyperfine constants of the sequence of four hydrocarbon radicals CH, C₂H, C₃H, and C₄H are briefly described.

Subject headings: interstellar: molecules — laboratory spectra — line identifications — molecular processes

The C₃H radical, a linear carbon chain with a $^2\Pi$ ground state, was recently identified in two astronomical sources, IRC +10216 and TMC-1 (Thaddeus *et al.* 1985), and in a laboratory discharge (Gottlieb *et al.* 1985, hereafter Paper I). Owing to the presence of both electronic orbital and spin angular momentum in the ground state, there are two parallel ladders of rotational transitions, and the Hamiltonian that describes the rotational spectrum is fairly complicated, with 14 coupling constants needed to fit the observed spin uncoupling, centrifugal distortion, lambda doubling, and hyperfine structure. Here we present the analysis in greater detail than in Paper I with a tabulation of the strongest C₃H rotational transitions likely to be useful to radio astronomy for frequencies less than 377 GHz.

In the last 15 years several approximate Hamiltonians for $^2\Pi$ molecules were derived, all adequately representing the available high precision beam maser and far-IR measurements of transitions in the OH, NO, SH, and CH radicals (for a detailed discussion see Brown *et al.* 1978 and Coxon *et al.* 1979). In our analysis we adopted the effective Hamiltonian of Brown *et al.* (1978, 1979) for a single vibrational level of a $^2\Pi$ state, which makes only implicit reference to admixtures with other vibrational and electronic states, and is therefore especially appropriate for C₃H, for which spectroscopic or theoretical information about excited states is not yet available. The

Hamiltonian of Brown *et al.* (1978, 1979) was derived from the fundamental molecular Hamiltonian, rather than on empirical grounds, so its parameters are associated with specific features of the energy-level structure and can be compared with *ab initio* calculations. Only the fourth-order lambda-doubling terms p_H and q_H were added empirically (Meerts 1977).

The Hamiltonian expressed as a 2×2 matrix (Table 1) was diagonalized numerically, and the parameters were fitted using the explicit expressions for the derivatives and the Marquardt algorithm (Bevington 1969) to obtain a least-squares estimation of the parameters. We tested our computer code by fitting the parameters given in Table 1 as well as d_D and C_I , to the OH data in Meerts, while A , γ , γ_D , B , and D , to which the OH microwave data are insensitive, were constrained to the values derived by Brown *et al.* (1981). The second- and third-order lambda-doubling and hyperfine parameters fitted agreed well with those of Brown *et al.* (1981), while the fourth-order lambda-doubling terms p_H and q_H agreed with Meerts's values. (Our C₃H data are insensitive to the higher order terms H , γ_D , C_I , $C_{I'}$, and d_D , so these have been omitted from our analysis.)

As discussed in Paper I, the C₃H frequencies listed in Table 2 were measured in a laboratory glow discharge through a flowing mixture of C₂H₂, He, and CO, except for the four hyperfine components of the $J = 3/2 \rightarrow 1/2$ transition, which were measured in the narrow-line astronomical source TMC-1 by Thaddeus *et al.* (1985). The widths (FWHM) of the TMC-1 lines were 40 kHz, while the widths of the laboratory lines

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MATRIX ELEMENTS OF THE HAMILTONIAN

| | $ ^2\Pi_{3/2}^\pm JIF\rangle$ | $ ^2\Pi_{1/2}^\pm JIF\rangle$ |
|---------------------------------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\langle ^2\Pi_{3/2}^\pm JIF \dots \dots \dots$ | $\frac{1}{2}A + Bz - Dz(z+1)$ $\mp \frac{1}{2}q_D xz$ $+ \frac{1}{2}(3a + \frac{3}{2}b_F + c)y$ | $-[B - \frac{1}{2}\gamma - 2Dx^2]$ $\mp \frac{1}{2}qx \mp \frac{1}{4}(p_D + 2q_D)x$ $\mp \frac{1}{2}q_D x^3 \mp q_H x^5$ $+ \frac{1}{2}(b_F - \frac{1}{3}c)y]z^{1/2}$ |
| $\langle ^2\Pi_{1/2}^\pm JIF \dots \dots \dots$ | ... | $-\frac{1}{2}A - \gamma + B(z+2)$ $-D(z^2 + 5z + 4)$ $\mp \frac{1}{2}(p + 2q)x \mp \frac{1}{4}(p_D + 2q_D)(x)(z+2)$ $\mp \frac{1}{2}q_D xz \mp p_H x^5$ $+ \frac{1}{2}(a - \frac{1}{2}b_F - \frac{1}{3}c \mp dx)y$ |

NOTE.—Here $x = J + \frac{1}{2}$; $z = (J - \frac{1}{2})(J + \frac{3}{2}) = (J + \frac{1}{2})^2 - 1$; $y = [F(F+1) - J(J+1) - I(I+1)]/[2J(J+1)]$; $b_F = b + c/3$.

TABLE 2
MEASURED CCCH REST FREQUENCIES

| $J \rightarrow J'$ | Ω | Lambda Component ^a | $F \rightarrow F'$ | Measured Frequencies ^b (MHz) | Measured minus Calculated ^c (MHz) |
|-------------------------------|----------|-------------------------------|--------------------|-----------------------------------------|----------------------------------------------|
| $3/2 \rightarrow 1/2$ | 1/2 | <i>a</i> | $2 \rightarrow 1$ | 32,627.300 | -0.001 |
| | | | $1 \rightarrow 0$ | 32,634.390 | 0.000 |
| | | <i>b</i> | $2 \rightarrow 1$ | 32,660.655 | 0.001 |
| | | | $1 \rightarrow 0$ | 32,663.375 | 0.000 |
| $5/2 \rightarrow 7/2$ | 3/2 | <i>a</i> | $3 \rightarrow 4$ | 80,388.107 | -0.006 |
| | | | $2 \rightarrow 3$ | 80,389.442 | 0.016 |
| | | <i>b</i> | $3 \rightarrow 4$ | 80,420.646 | -0.056 |
| | | | $2 \rightarrow 3$ | 80,422.052 | -0.038 |
| $7/2 \rightarrow 9/2$ | 1/2 | <i>b</i> | $4 \rightarrow 5$ | 97,995.166 | -0.008 |
| | | | $3 \rightarrow 4$ | 97,995.913 | -0.016 |
| | | <i>a</i> | $4 \rightarrow 5$ | 98,011.611 | 0.015 |
| | | | $3 \rightarrow 4$ | 98,012.524 | -0.014 |
| $7/2 \rightarrow 9/2$ | 3/2 | <i>a</i> | $4 \rightarrow 5$ | 103,319.276 | -0.033 |
| | | | $3 \rightarrow 4$ | 103,319.786 | -0.040 |
| | | <i>b</i> | $4 \rightarrow 5$ | 103,372.483 | -0.016 |
| | | | $3 \rightarrow 4$ | 103,373.094 | -0.015 |
| $9/2 \rightarrow 11/2$ | 1/2 | <i>b</i> | $5 \rightarrow 6$ | 119,804.682 | 0.014 |
| | | | $4 \rightarrow 5$ | 119,805.322 | 0.004 |
| | | <i>a</i> | $5 \rightarrow 6$ | 119,847.476 | 0.034 |
| | | | $4 \rightarrow 5$ | 119,858.259 | 0.007 |
| $11/2 \rightarrow 13/2$ | 1/2 | * | $6 \rightarrow 7$ | 141,635.793 | -0.033 |
| | | | $5 \rightarrow 6$ | 141,636.431 | 0.031 |
| | | * | $6 \rightarrow 7$ | 141,708.728 | -0.023 |
| | | | $5 \rightarrow 6$ | 141,709.494 | 0.016 |
| $11/2 \rightarrow 13/2$ | 3/2 | <i>a</i> | $5 \rightarrow 6$ | 149,106.972 | 0.069 |
| | | | $6 \rightarrow 7$ | 149,212.667 | 0.090 |
| | | <i>b</i> | $5 \rightarrow 6$ | 149,212.667 | 0.090 |
| | | | $6 \rightarrow 7$ | 149,212.667 | 0.090 |
| $13/2 \rightarrow 15/2$ | 1/2 | <i>a</i> | $7 \rightarrow 8$ | 163,491.035 | -0.012 |
| | | | $6 \rightarrow 7$ | 163,491.557 | -0.002 |
| | | <i>b</i> | $7 \rightarrow 8$ | 163,597.232 | -0.033 |
| | | | $6 \rightarrow 7$ | 163,597.900 | -0.033 |
| $13/2 \rightarrow 15/2$ | 3/2 | <i>a</i> | $6 \rightarrow 7$ | 171,958.650 | 0.055 |
| | | | $7 \rightarrow 8$ | 172,094.778 | 0.059 |
| | | <i>b</i> | $6 \rightarrow 7$ | 172,094.778 | 0.059 |
| | | | $7 \rightarrow 8$ | 172,094.778 | 0.059 |
| $15/2 \rightarrow 17/2$ | 1/2 | <i>a</i> | $8 \rightarrow 9$ | 185,371.952 | 0.004 |
| | | | $7 \rightarrow 8$ | 185,372.417 | 0.009 |
| | | <i>b</i> | $8 \rightarrow 9$ | 185,513.968 | 0.019 |
| | | | $7 \rightarrow 8$ | 185,514.589 | 0.021 |
| $15/2 \rightarrow 17/2$ | 3/2 | <i>a</i> | $7 \rightarrow 8$ | 194,780.373 | -0.062 |
| | | | $8 \rightarrow 9$ | 194,948.795 | -0.071 |
| | | <i>b</i> | $7 \rightarrow 8$ | 194,948.795 | -0.071 |
| | | | $8 \rightarrow 9$ | 194,948.795 | -0.071 |

^a Following the convention of Brown *et al.* (1975), a transition between lambda doublets of lower energy is designated as an *a* component and between upper doublets as a *b* component. The asterisk denotes that the order reverses in the $^2\Pi_{1/2}$ ladder between $J = 11/2$ and $J = 13/2$.

^b Estimated 1 σ uncertainties: ± 15 kHz for the $J = 3/2 \rightarrow 1/2$ transitions in TMC-1 (Thaddeus *et al.* 1985), except for the 32634 MHz transition, where the uncertainty was 20 kHz, while the uncertainty for all the other transitions was 50 kHz.

^c Calculated with the recommended constants in Table 3. The radial velocity in TMC-1, treated as a free parameter in the analysis, was $V_{\text{LSR}} = 5.3 \pm 0.3$ km s⁻¹.

varied between 800 and 1200 kHz. The estimated 50 kHz uncertainty in the frequencies is somewhat larger than for other transient species recently studied in this laboratory, owing to the presence of small or unresolved hyperfine structure in the $^2\Pi_{3/2}$ spectra and to the ineffectiveness of Zeeman modulation (because of a small *g*-factor) in removing baseline distortion from standing waves in the $^2\Pi_{1/2}$ spectra. (See Paper I for the assignment of the C₃H millimeter-wave spectrum and the determination of the parameters required to reproduce the measured frequencies.)

The recommended spectroscopic constants shown in Table 3 were determined from a simultaneous least-squares fit to the frequencies in Table 2 weighted by the inverse square of the uncertainties. The square root of the reduced χ^2 , *S*, defined as $S = [\chi^2/(N - m)]^{1/2}$, where *N* is the number of measurements (38) and *m* the number of parameters (15), was 0.88, as compared with an expected value of about unity in the absence of systematic errors (Cohen and DuMond 1957). There is therefore no evidence for missing terms in the Hamiltonian or systematic errors in the measured line frequencies.

In a few cases the correlation coefficients, shown in Table 4, are greater than 0.90. Correlations between the lambda-doubling terms can be reduced substantially if $p + 2q$ and $p_D + 2q_D$ are fitted, rather than p and p_D , although in both cases the values of the parameters and of *S* remain the same. The strongest correlation is between *A* and γ , with correlation coefficient near unity (-0.9996). The possibility of theoretical indeterminacies arises in the Hamiltonian of Brown *et al.* because different terms can make indistinguishable contributions to the eigenvalues. When two parameters are correlated, the usual practice is to constrain one *a priori*. The spin-orbit constant in $^2\Pi$ molecules is generally constrained to the value determined from optical data or from laser magnetic resonance (LMR) spectroscopy. It was necessary, in the absence of any spectroscopic data on C₃H other than our own, to include *A* in the least-squares fit. If γ is constrained to be zero, *S* is much larger (1.51). The values of *A* and γ may change by more than the standard deviation when measurements at other wavelengths are made.

The rotational spectrum of C₃H up to 376 GHz given in Table 5 (i.e., well into the far-IR) is calculated from the best-fitted spectroscopic constants and the correlation coefficient

TABLE 3
SPECTROSCOPIC CONSTANTS FOR CCCH
IN THE $X ^2\Pi$ STATE

| Constant | Value |
|-----------------------------|-----------------------|
| A_{eff} | 430828 ± 41 |
| B | 11186.335 ± 0.002 |
| $D \times 10^3$ | 5.55 ± 0.02 |
| γ_{eff} | 36.9 ± 1.1 |
| p | -7.20 ± 0.07 |
| q | -16.62 ± 0.03 |
| $p_D \times 10^3$ | 47.4 ± 2.4 |
| $q_D \times 10^3$ | 1.6 ± 0.6 |
| $p_H \times 10^6$ | 45 ± 6 |
| $q_H \times 10^6$ | 3.1 ± 2.1 |
| a | 12.3 ± 0.2 |
| $b + c/3$ | -13.8 ± 0.6 |
| c | 28.3 ± 1.4 |
| d | 16.2 ± 0.1 |

NOTE.—Units are MHz. Uncertainties are 1 σ , derived from a least-squares fit.

TABLE 4
CORRELATION COEFFICIENT MATRIX

| | <i>A</i> | <i>B</i> | <i>D</i> | γ | <i>p</i> | <i>p_D</i> | <i>p_H</i> | <i>q</i> | <i>q_D</i> | <i>q_H</i> | <i>a</i> | <i>b_F</i> | <i>c</i> | <i>d</i> | <i>V_{Lsr}</i> |
|------------------------------|----------|----------|----------|----------|----------|----------------------|----------------------|----------|----------------------|----------------------|----------|----------------------|----------|----------|------------------------|
| <i>A</i> | 1.00 | -0.03 | -0.07 | -1.00 | 0.02 | 0.00 | 0.01 | -0.02 | -0.01 | 0.01 | 0.16 | -0.07 | 0.13 | 0.00 | 0.32 |
| <i>B</i> | | 1.00 | 0.93 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.18 | 0.08 | -0.14 | 0.00 | 0.40 |
| <i>D</i> | | | 1.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.16 | 0.07 | -0.12 | 0.00 | 0.36 |
| γ | | | | 1.00 | -0.02 | 0.00 | -0.01 | 0.02 | 0.01 | -0.01 | -0.16 | 0.07 | -0.13 | 0.00 | -0.31 |
| <i>p</i> | | | | | 1.00 | -0.94 | 0.27 | -0.89 | 0.83 | -0.72 | 0.00 | 0.00 | 0.00 | -0.29 | 0.01 |
| <i>p_D</i> | | | | | | 1.00 | -0.35 | 0.93 | -0.87 | 0.76 | 0.00 | 0.00 | 0.00 | 0.08 | 0.00 |
| <i>p_H</i> | | | | | | | 1.00 | -0.06 | -0.13 | 0.32 | 0.00 | 0.00 | 0.00 | -0.22 | 0.00 |
| <i>q</i> | | | | | | | | 1.00 | -0.96 | 0.87 | -0.01 | 0.00 | 0.00 | -0.07 | -0.01 |
| <i>q_D</i> | | | | | | | | | 1.00 | -0.97 | 0.00 | 0.00 | 0.00 | 0.08 | 0.00 |
| <i>q_H</i> | | | | | | | | | | 1.00 | 0.00 | 0.00 | 0.00 | -0.08 | 0.00 |
| <i>a</i> | | | | | | | | | | | 1.00 | -0.20 | 0.57 | 0.02 | -0.18 |
| <i>b_F</i> | | | | | | | | | | | | 1.00 | -0.91 | 0.00 | 0.58 |
| <i>c</i> | | | | | | | | | | | | | 1.00 | 0.00 | -0.58 |
| <i>d</i> | | | | | | | | | | | | | | 1.00 | -0.03 |
| <i>V_{Lsr}</i> | | | | | | | | | | | | | | | 1.00 |

TABLE 5
CALCULATED ROTATIONAL SPECTRUM OF C₃H

| J + J' | 2 ₁ 1/2 | | | | | 2 ₃ 3/2 | | | | | |
|-------------|--------------------|---------|-----------------|--------|---------|--------------------|--------|-----------------|-----------------|------|---------|
| | F → F' | Λ Comp. | Frequency (MHz) | Unc. | E/k (K) | S | F → F' | Λ Comp. | Frequency (MHz) | Unc. | E/k (K) |
| 1/2 + 3/2 | 1 + 1 | a | 32616.989 (98) | 0.00 | 0.17 | | | | | | |
| | 1 + 2 | | 32627.255 (16) | 0.00 | 0.83 | | | | | | |
| | 0 + 1 | | 32634.344 (23) | 0.00 | 0.33 | | | | | | |
| | 1 + 2 | b | 32660.608 (16) | 0.00 | 0.83 | | | | | | |
| | 0 + 1 | | 32663.329 (20) | 0.00 | 0.33 | | | | | | |
| | 1 + 1 | | 32667.633 (96) | 0.00 | 0.17 | | | | | | |
| 3/2 + 5/2 | 2 + 3 | a | 54405.258 (20) | 1.57 | 1.40 | 2 + 3 | a | 57436.320 (35) | 21.26 | 0.93 | |
| | 1 + 2 | | 54407.222 (18) | 1.57 | 0.90 | 1 + 2 | | 57439.844 (69) | 21.26 | 0.60 | |
| | 2 + 3 | b | 54427.591 (20) | 1.57 | 1.40 | 2 + 3 | b | 57452.874 (35) | 21.26 | 0.93 | |
| | 1 + 2 | | 54428.881 (18) | 1.57 | 0.90 | 1 + 2 | | 57456.452 (69) | 21.26 | 0.60 | |
| 5/2 + 7/2 | 3 + 4 | a | 76198.658 (23) | 4.18 | 1.92 | 3 + 4 | a | 80388.113 (28) | 24.02 | 1.61 | |
| | 2 + 3 | | 76199.865 (23) | 4.18 | 1.43 | 2 + 3 | | 80389.426 (32) | 24.02 | 1.19 | |
| | 3 + 4 | b | 76204.146 (23) | 4.18 | 1.92 | 3 + 4 | b | 80420.702 (28) | 24.02 | 1.61 | |
| | 2 + 3 | | 76205.072 (23) | 4.18 | 1.43 | 2 + 3 | | 80422.090 (32) | 24.02 | 1.19 | |
| 7/2 + 9/2 | 4 + 5 | b | 97995.174 (25) | 7.84 | 2.44 | 4 + 5 | a | 103319.309 (27) | 27.87 | 2.20 | |
| | 3 + 4 | | 97995.929 (25) | 7.84 | 1.94 | 3 + 4 | | 103319.826 (27) | 27.87 | 1.75 | |
| | 4 + 5 | a | 98011.596 (25) | 7.83 | 2.44 | 4 + 5 | b | 103372.498 (27) | 27.88 | 2.20 | |
| | 3 + 4 | | 98012.538 (25) | 7.83 | 1.94 | 3 + 4 | | 103373.109 (27) | 27.88 | 1.75 | |
| 9/2 + 11/2 | 5 + 6 | b | 119804.668 (23) | 12.54 | 2.95 | 5 + 6 | a | 126226.490 (25) | 32.83 | 2.76 | |
| | 4 + 5 | | 119805.318 (23) | 12.54 | 2.45 | 4 + 5 | | 126226.635 (25) | 32.83 | 2.29 | |
| | 5 + 6 | a | 119847.442 (23) | 12.54 | 2.95 | 5 + 6 | b | 126304.247 (25) | 32.84 | 2.76 | |
| | 4 + 5 | | 119848.252 (23) | 12.54 | 2.45 | 4 + 5 | | 126304.501 (25) | 32.84 | 2.29 | |
| 11/2 + 13/2 | 6 + 7 | * | 141635.826 (22) | 18.29 | 3.45 | 5 + 6 | a | 149106.874 (26) | 38.89 | 2.82 | |
| | 5 + 6 | | 141636.400 (22) | 18.29 | 2.96 | 6 + 7 | | 149106.928 (26) | 38.89 | 3.30 | |
| | 6 + 7 | * | 141708.751 (22) | 18.29 | 3.45 | 6 + 7 | b | 149212.545 (27) | 38.90 | 3.30 | |
| | 5 + 6 | | 141709.478 (22) | 18.29 | 2.96 | 5 + 6 | | 149212.615 (27) | 38.90 | 2.82 | |
| 13/2 + 15/2 | 7 + 8 | a | 163491.047 (23) | 25.09 | 3.96 | 6 + 7 | a | 171958.507 (29) | 46.04 | 3.35 | |
| | 6 + 7 | | 163491.559 (23) | 25.09 | 3.46 | 7 + 8 | | 171958.673 (29) | 46.05 | 3.83 | |
| | 7 + 8 | b | 163597.265 (23) | 25.09 | 3.96 | 6 + 7 | b | 172094.703 (29) | 46.06 | 3.35 | |
| | 6 + 7 | | 163597.933 (23) | 25.09 | 3.46 | 7 + 8 | | 172094.733 (29) | 46.06 | 3.83 | |
| 15/2 + 17/2 | 8 + 9 | a | 185371.948 (33) | 32.93 | 4.46 | 7 + 8 | a | 194780.312 (44) | 54.30 | 3.86 | |
| | 7 + 8 | | 185372.408 (33) | 32.93 | 3.96 | 8 + 9 | | 194780.543 (44) | 54.30 | 4.35 | |
| | 8 + 9 | b | 185513.949 (33) | 32.94 | 4.46 | 7 + 8 | b | 194948.821 (44) | 54.32 | 3.86 | |
| | 7 + 8 | | 185514.568 (33) | 32.94 | 3.96 | 8 + 9 | | 194948.906 (44) | 54.32 | 4.35 | |
| 17/2 + 19/2 | 9 + 10 | a | 207279.428 (95) | 41.83 | 4.96 | 8 + 9 | a | 217571.79 (12) | 63.64 | 4.38 | |
| | 8 + 9 | | 207279.842 (95) | 41.83 | 4.47 | 9 + 10 | | 217572.06 (12) | 63.65 | 4.89 | |
| | 9 + 10 | b | 207459.069 (94) | 41.84 | 4.96 | 8 + 9 | b | 217773.75 (12) | 63.67 | 4.38 | |
| | 8 + 9 | | 207459.646 (94) | 41.84 | 4.47 | 9 + 10 | | 217773.87 (12) | 63.67 | 4.89 | |
| 19/2 + 21/2 | 10 + 11 | a | 229213.75 (25) | 51.78 | 5.47 | 9 + 10 | a | 240333.06 (30) | 74.09 | 4.89 | |
| | 9 + 10 | | 229214.13 (25) | 51.78 | 4.97 | 10 + 11 | | 240333.34 (30) | 74.09 | 5.38 | |
| | 10 + 11 | b | 229432.29 (25) | 51.80 | 5.47 | 9 + 10 | b | 240568.91 (30) | 74.12 | 4.89 | |
| | 9 + 10 | | 229432.82 (25) | 51.80 | 4.97 | 10 + 11 | | 240569.04 (30) | 74.12 | 5.38 | |
| 21/2 + 23/2 | 11 + 12 | a | 251174.66 (56) | 62.78 | 5.97 | 10 + 11 | a | 263064.72 (63) | 85.62 | 5.40 | |
| | 10 + 11 | | 251174.99 (56) | 62.78 | 5.47 | 11 + 12 | | 263065.02 (63) | 85.62 | 5.89 | |
| | 11 + 12 | b | 251432.77 (55) | 62.81 | 5.97 | 10 + 11 | b | 263334.23 (64) | 85.67 | 5.40 | |
| | 10 + 11 | | 251433.27 (55) | 62.81 | 5.47 | 11 + 12 | | 263334.36 (64) | 85.67 | 5.89 | |
| 23/2 + 25/2 | 12 + 13 | a | 273161.5 (11) | 74.83 | 6.47 | 11 + 12 | a | 285767.8 (12) | 98.24 | 5.91 | |
| | 11 + 12 | | 273161.8 (11) | 74.83 | 5.97 | 12 + 13 | | 285768.1 (12) | 98.24 | 6.40 | |
| | 12 + 13 | b | 273459.3 (11) | 74.88 | 6.47 | 11 + 12 | b | 286070.1 (12) | 98.31 | 5.91 | |
| | 11 + 12 | | 273459.8 (11) | 74.88 | 5.97 | 12 + 13 | | 286070.2 (12) | 98.31 | 6.40 | |
| 25/2 + 27/2 | 13 + 14 | a | 295173.2 (19) | 87.94 | 6.97 | 12 + 13 | a | 308443.6 (21) | 111.96 | 6.41 | |
| | 12 + 13 | | 295173.5 (19) | 87.94 | 6.47 | 13 + 14 | | 308443.9 (21) | 111.96 | 6.91 | |
| | 13 + 14 | b | 295510.3 (19) | 88.00 | 6.97 | 12 + 13 | b | 308777.1 (21) | 112.04 | 6.41 | |
| | 12 + 13 | | 295510.8 (19) | 88.00 | 6.47 | 13 + 14 | | 308777.2 (21) | 112.04 | 6.91 | |
| 27/2 + 29/2 | 14 + 15 | a | 317208.6 (31) | 102.11 | 7.47 | 13 + 14 | a | 331093.7 (34) | 126.76 | 6.92 | |
| | 13 + 14 | | 317208.8 (31) | 102.11 | 6.97 | 14 + 15 | | 331094.0 (34) | 126.76 | 7.42 | |
| | 14 + 15 | b | 317584.2 (31) | 102.18 | 7.47 | 13 + 14 | b | 331456.2 (34) | 126.85 | 6.92 | |
| | 13 + 14 | | 317584.6 (31) | 102.18 | 6.97 | 14 + 15 | | 331456.3 (34) | 126.85 | 7.42 | |

TABLE 5—Continued

| $^2\Pi_{1/2}$ | | | | | | | $^2\Pi_{3/2}$ | | | | | | |
|---------------|---------|-----------|--------------------|------|--------|------|---------------|-----------|--------------------|------|--------|------|--|
| J + J' | F + F' | Λ | Frequency (MHz) | Unc. | E/k | | F + F' | Λ | Frequency (MHz) | Unc. | E/k | | |
| | | | | | Comp. | (K) | | | | | (K) | S | |
| 29/2 + 31/2 | 15 + 16 | a | 339266.4 | (49) | 117.33 | 7.97 | 14 + 15 | a | 353719.7 | (52) | 142.65 | 7.43 | |
| | 14 + 15 | | 339266.6 | (49) | 117.33 | 7.47 | | | 353720.0 | (52) | 142.65 | 7.92 | |
| | 15 + 16 | b | 339678.9 | (49) | 117.42 | 7.97 | | b | 354108.3 | (53) | 142.76 | 7.43 | |
| | 14 + 15 | | 339679.3 | (49) | 117.42 | 7.47 | | | 354108.4 | (53) | 142.76 | 7.92 | |
| 31/2 + 33/2 | 16 + 17 | a | 361345.1 | (74) | 133.61 | 8.47 | 15 + 16 | a | 376323.4 | (78) | 159.62 | 7.93 | |
| | 15 + 16 | | 361345.3 | (74) | 133.61 | 7.98 | | | 376323.6 | (78) | 159.62 | 8.43 | |
| | 16 + 17 | b | 361792.7 | (73) | 133.72 | 8.47 | | b | 376734.5 | (79) | 159.75 | 7.93 | |
| | 15 + 16 | | 361793.1 | (73) | 133.72 | 7.98 | | | 376734.6 | (79) | 159.75 | 8.43 | |

NOTE.—Shown in parentheses are the 1σ uncertainties. E is the energy of the lower state. Only those hyperfine components with relative intensity greater than 0.05 are tabulated.

TABLE 6
HYPERFINE AND MOLECULAR CONSTANTS OF CARBON CHAIN RADICALS

| RADICAL | STATE | HYPERFINE PARAMETERS (MHz) ^a | | | | MOLECULAR CONSTANTS (10^{24} cm^{-3}) | | | | REFERENCE |
|-------------|-------------|-----------------------------------------|----------------|------------|-------------|---------------------------------------------------|---------------------------------------------|-------------------------------------|-----------------------------|-----------|
| | | <i>a</i> | <i>b + c/3</i> | <i>c</i> | <i>d</i> | $\langle 1/r^3 \rangle$ | $\langle (3 \cos^2 \theta - 1)/r^3 \rangle$ | $\langle \sin^2 \theta/r^3 \rangle$ | $\langle \psi^2(0) \rangle$ | |
| CH | $X^2\Pi$ | 54.188(96) | -57.71(11) | 56.98(15) | 43.4812(17) | 0.6862 | 0.4810 | 0.3671 | -0.0872 | 1 |
| CCH | $X^2\Sigma$ | ... | 44.511(17) | 12.254(26) | ... | ... | 0.1035 | ... | 0.0673 | 2 |
| CCCH | $X^2\Pi$ | 12.3(2) | -13.8(6) | 28.3(14) | 16.2(1) | 0.1558 | 0.2389 | 0.1368 | -0.0208 | 3 |
| CCCCH | $X^2\Sigma$ | ... | -14.943(7) | 12.435(10) | ... | ... | 0.1050 | ... | -0.0226 | 4 |

^a Shown in parentheses are the 1σ uncertainties.

REFERENCES.—(1) Bogey, Demuynck, and Destombes 1983; (2) Gottlieb, Gottlieb, and Thaddeus 1983; (3) this work; (4) Gottlieb *et al.* 1983.

matrix. The uncertainties (in parentheses) were calculated from the standard deviation of parameters and the correlation coefficients, using the generalized law for the propagation of errors (Cohen and DuMond 1957). The major source of uncertainty is q_H , which is poorly determined in our analysis. The rotational line strengths were calculated in the intermediate coupling case.

With our data and those of Bogey, Demuynck, and Desombes (1983) for CH, a comparison of the hyperfine constants of the four simplest carbon chain radicals, CH, CCH, CCCH, and CCCCH, is now possible and is given in Table 6. The Frosch and Foley hyperfine parameters *a*, *c*, and *d* are proportional to r^{-3} , so we can now test how well the approximation that places the unpaired electron in a $2p\pi$ orbital centered on a carbon atom applies to C_3H by scaling *c(CH)*

and *d(CH)* by the ratio *a(C₃H)/a(CH)*: they are found to agree with the measured values to within a factor of 2. The *ab initio* values for *c* and *d* (Green 1980) agree better with the values deduced from CH than with the measured values; Green suggests (personal communication) that the very close agreement of the Fermi contact terms (*b_F*) for C_3H and C_4H is partly fortuitous. The molecular parameters calculated from the measured hyperfine constants, $\langle 1/r^3 \rangle$, $\langle \sin^2 \theta/r^3 \rangle$, $\langle (3 \cos^2 \theta - 1)/r^3 \rangle$, and $\langle \psi^2(0) \rangle$ (Table 6), are very sensitive to the electron distribution and provide stringent tests of the molecular wave functions.

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REFERENCES

- Bevington, P. R. 1969, *Data Reduction and Error Analysis for the Physical Sciences* (New York: McGraw-Hill).
- Bogey, M., Demuynck, C., and Destombes, J. L. 1983, *Chem. Phys. Letters*, **100**, 105.
- Brown, J. M., *et al.* 1975, *J. Molec. Spectrosc.*, **55**, 500.
- Brown, J. M., Colbourne, E. A., Watson, J. K. G., and Wayne, F. D. 1979, *J. Molec. Spectrosc.*, **74**, 294.
- Brown, J. M., Kaise, M., Kerr, C. M. L., and Milton, D. J. 1978, *Molec. Phys.*, **36**, 553.
- Brown, J. M., Kerr, C. M. L., Wayne, F. D., Evenson, K. M., and Radford, H. E. 1981, *J. Molec. Spectrosc.*, **86**, 544.
- Cohen, E. R., and DuMond, J. W. M. 1957, in *Handbuch der Physik*, ed. S. Flügge (Berlin: Springer), **35**, 1.
- Coxon, J. A., Sastry, K. V. L. N., Austin, J. A., and Levy, D. H. 1979, *Canadian J. Phys.*, **57**, 619.
- Gottlieb, C. A., Gottlieb, E. W., and Thaddeus, P. 1983, *Ap. J.*, **264**, 740.
- Gottlieb, C. A., Gottlieb, E. W., Thaddeus, P., and Kawamura, H. 1983, *Ap. J.*, **275**, 916.
- Gottlieb, C. A., Vrtilek, J. M., Gottlieb, E. W., Thaddeus, P., and Hjalmarson, Å. 1985, *Ap. J. (Letters)*, **294**, L55 (Paper I).
- Green, S. 1980, *Ap. J.*, **240**, 962.
- Meerts, W. L. 1977, *Chem. Phys. Letters*, **46**, 24.
- Thaddeus, P., Gottlieb, C. A., Hjalmarson, Å., Johannsson, L. E. B., Irvine, W. M., Friberg, P., and Linke, R. A. 1985, *Ap. J. (Letters)*, **294**, L49.

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